

Chemistry of Rubber Processing and Disposal

by Robert L. Bebb*

The major chemical changes during the processing of rubber occur with the breakdown in mastication and during vulcanization of the molded tire. There is little chemical change during the compounding, calendering, extrusion, and molding steps. Reclaiming is the process of converting scrap rubber into an unsaturated, processible product that can be vulcanized with sulfur. Pyrolysis of scrap rubber yields a complex mixture of liquids, gas, and residue in varying ratios dependent on the nature of the scrap and the conditions of pyrolysis.

The literature has little information on the chemistry of rubber processing and disposal; it has been necessary to draw from various sources to develop a picture of the chemical events that may occur. This review is limited to natural rubber and to the important synthetic rubbers of the tire industry.

Processing

Rubber processing consists of operations performed on materials or systems to increase their utility through chemical reaction, flow, or permanent change in a physical property (1). The major processing steps wherein most chemical changes occur in tire production are: polymer breakdown by mastication on a mill or in a Banbury, extrusion, calendering, and curing. The tire building process and molding in the curing operation do not normally involve chemical reactions.

Mastication

In 1820 Hancock discovered the effect of mastication on rubber. The process has become basic in the commercial processing of rubber. Mastication gradually renders the rubber more plastic and decreases its solution viscosity.

It is now known that the high molecular weight of rubber is reduced during this degradation. Even a light mastication can reduce

the molecular weight to one-tenth its initial level.

Hancock had softened rubber in an oven and later had used steam for the purpose. Over the years it has been determined that heat alone is not the cause, for cold mastication is even more effective than warm milling, and both hot and cold milling are more effective than heat alone.

The autoxidation of natural rubber was first studied in 1861, when the deterioration of gutta percha was attributed to oxidation. Progress on the subject was complicated by normal antioxidants carried with rubber from the tree and traces of different impurities that act as catalysts (2). It was further complicated by the action of ultraviolet light in accelerating oxidation.

The harmful proportion of oxygen is extremely slight; less than 1% in a vulcanizate produces quite obvious changes. Fortunately, crude rubber, which has a greater sensitivity toward oxygen, is normally well supplied with natural antioxidants.

In 1921 workers at the Research Association of British Rubber Manufacturers reported that the softening effect produced by milling can also be observed by heating rubber in air or oxygen. There was little softening in the absence of oxygen (Fig. 1).

Repeated passes of natural rubber through a tight mill showed a significant drop in viscosity (Fig. 2).

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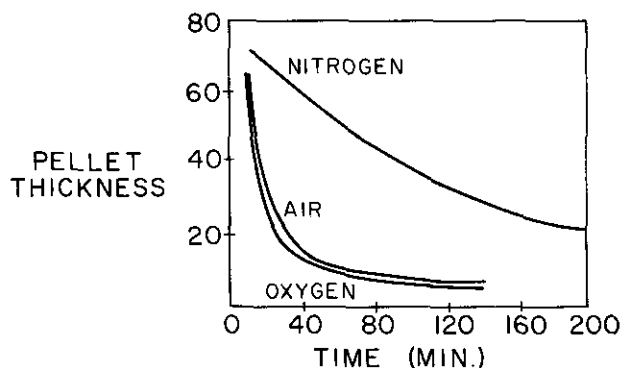


FIGURE 1. Effect of oxygen in mastication.

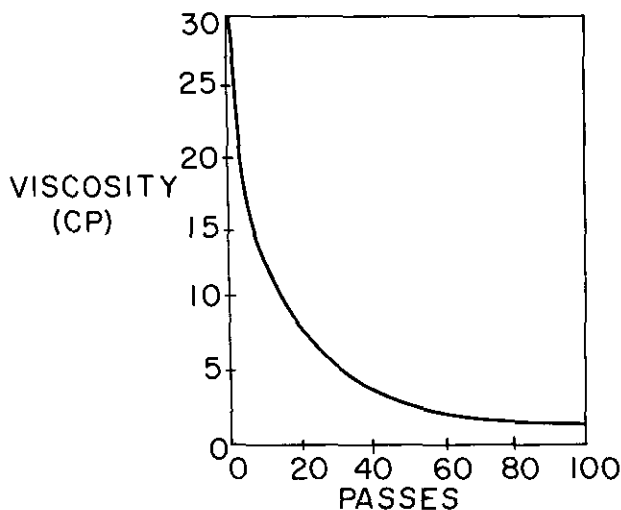


FIGURE 2. Plasticity vs. mill passes.

Concurrent work by Busse and by Cotton (3-6) identified the dependence of softening during mastication on the presence of air, oxygen, or ozone. Volatile aldehydes were evolved during mastication in air, and in 140 min natural rubber increased in weight by 0.32%. These workers attributed part of the increase in nitrogen to air dissolved in the sample (Fig. 2).

Both hot and cold mastication were more efficient than warm mastication (ca. 115°C) (Fig. 3), and two mechanisms have been proposed for the "cold" (below 100°C) and "hot" (above 130°C) conditions (7).

Oxidation is held responsible for "hot" breakdown in the presence of oxygen (Fig. 4).

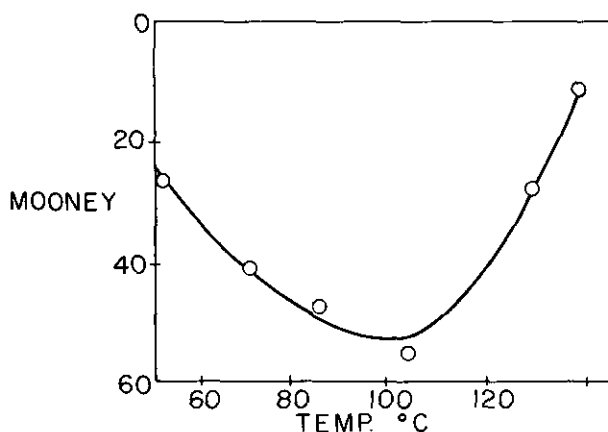


FIGURE 3. Mastication vs. temperature.

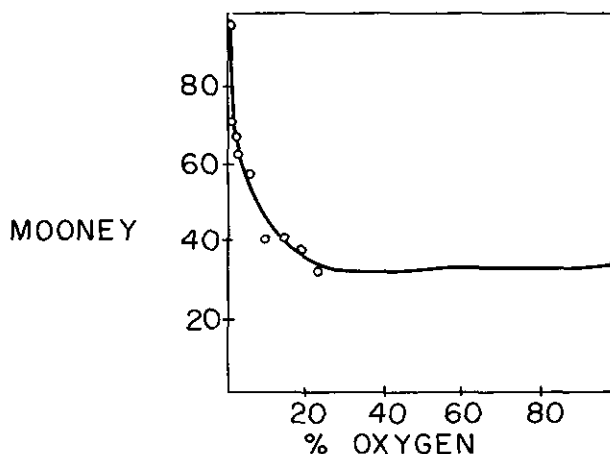
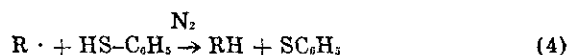


FIGURE 4. Oxygen concentration vs. mastication.

At low temperatures, the chain is ruptured at primary bonds through stresses set up in mastication. The rubber is compressed, stretched, squeezed, sheared in rapid succession and free radicals are produced. These recombine, unless some other substance (e.g., quinones, thiols, disulfides) is present to serve as a free-radical acceptor.

Mastication in an inert atmosphere leads to breakdown as long as a radical acceptor is present [Eqs. (1)-(4)]. This was shown with 1% thiophenol [Eq. (4)]. Radical acceptors are effective only in "cold" mastication in the absence of oxygen and depend on the mechanical rupture which is significant only at lower

temperatures. As the rubber becomes softer, fewer ruptures occur.



It is further possible that addition products react with other fragments to build up, rather than decrease the chain length or to crosslink to form gel.

Some chemical plasticizers (peptizers) accelerate breakdown. These are not radical acceptors but are oxidation catalysts (copper naphthenate) and are normally effective only above 100°C.

An interesting application of oxidative softening has been used in the German synthetic rubber industry (8). Immediately before it was used, Buna S was exposed in crumb or noodle form to an oxygen atmosphere at 130–135°C. The rubber softened during this step and could be brought to the plasticity needed by the users. The softened rubber had to be used within a short time (24 hr); otherwise it rapidly became stiffer than the original rubber and could not be resoftened. Here again, the softening was dependent on oxygen; it would not proceed in its absence (8).

When butadiene-styrene rubber (GR-S) was introduced during World War II, its response to milling was found to be different from that of natural rubber, and factory and labor problems arose. While GR-S had a lower initial plasticity than natural rubber, it softened more slowly during conventional milling.

GR-S can be softened by oven aging but, as in the case of the Buna S, once this process starts it continues to a resinous state. Here the processes of chain scission and crosslinking compete at rates dependent on temperature.

The various rubbers have shown that the greater the unsaturation, the greater the sensitivity toward oxidation. Natural rubber retains some natural antioxidants from the tree and is storage-stable, but antioxidants must be added during the manufacture of synthetic rubber for shelf and processing stability. Among the synthetic rubbers, the butadiene and isoprene polymers are more sensitive to oxidation than Butyl rubber (containing iso-

prene) and much more than ethylene-propylene-based rubbers.

Natural rubber and Butyl rubber undergo chain scission to weak stocks with surface tack. Chemical analysis shows that every possible oxygen-containing functional group is present. Butadiene-styrene and butadiene-acrylonitrile rubbers undergo chain crosslinking, becoming increasingly boardy, inflexible, "short", and free of tackiness.

A field receiving considerable study is the formation of interpolymers through the action of mastication (9, 10). In a nitrogen atmosphere, interpolymers have been made from natural and synthetic rubber as well as copolymers of these with phenolic resins. For instance, when Neoprene and natural rubber are masticated in the usual way, a simple mixture occurs. In a nitrogen atmosphere, the rubber becomes bound to the Neoprene so that the product responds to a typical Neoprene cure, although the mixture does not.

Vulcanization

Vulcanization is the process of treating natural or synthetic rubber with a chemical, usually sulfur, a sulfur-containing compound, or a peroxide, so as to impart improved properties, such as better elasticity, lower plasticity, or more resistance to solvent action.

Few rubber products are used in the unvulcanized state, and only a limited amount of rubber goes into pure gum stocks. Therefore, the blending of rubbers, alone or in mixtures, with reinforcing agents, fillers, and cure systems must be carefully controlled in the manufacture of high quality rubber products.

The classic procedure for compounding rubber has mixed baled rubber on a mill or in an enclosed mixer. As synthetic rubber has become available at a practical price in powder, solution, or latex form, novel methods of incorporating compounding ingredients have been investigated, but the established routes of mixing conventional rubbers will be changed only if some outstanding price or property advantage results.

Sulfur and sulfur-liberating compounds are most often involved in commercial vulcanization but crosslinking can also be obtained with radiation and with compounds that decompose at curing temperatures to yield free radicals, oxidants of appropriate resonance structure, or

Table 1. Curing agents and crosslinks they produce.

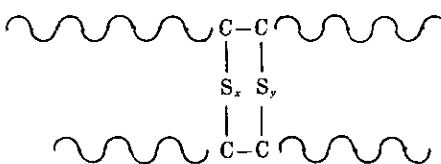
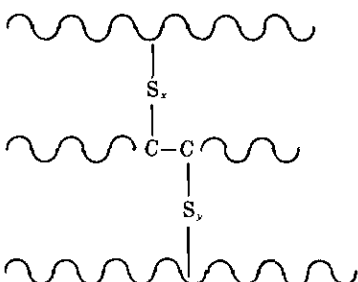
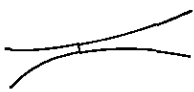
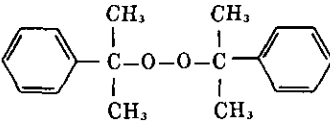
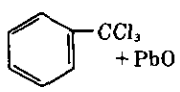
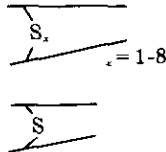
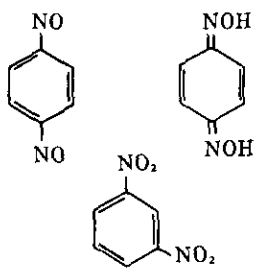
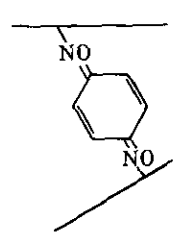
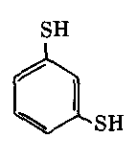
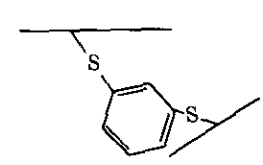
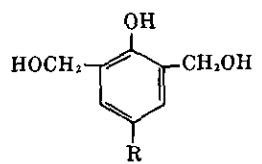
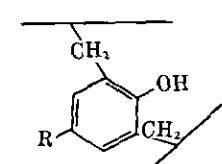
Curing agent	Crosslink type
	Sulfur linkages
	
	
Free radical generators	C - C crosslinks
Gamma rays	
	
Dicumyl peroxide	
 + PbO	
Benzotrichloride + litharge	
Bivalent atoms or radicals	Bridge type crosslinks
$ \begin{array}{c} \text{CH}_3 \quad \text{S} \quad \text{S} \quad \text{CH}_3 \\ \diagdown \quad \parallel \quad \parallel \quad \diagup \\ \text{N} - \text{C} - \text{S} - \text{S} - \text{C} - \text{N} \\ \diagup \quad \parallel \quad \parallel \quad \diagdown \\ \text{CH}_3 \quad \text{S} \quad \text{S} \quad \text{CH}_3 \end{array} $	

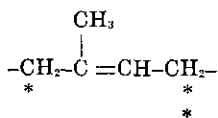
Table 1. Curing agents and crosslinks they produce.—Continued.

Curing agent	Crosslink type
 <p> <chem>O=[N+]([O-])c1ccc([N+](=O)[O-])cc1</chem> <chem>O=[N+]([O-])c1ccccc1O</chem> <chem>O=[N+]([O-])c1ccccc1O</chem> </p>	
 <p> <chem>SC1=CC=C(S)C=C1</chem> </p>	
 <p> <chem>OC1=C(CO)C(=C(CO)C1)O</chem> </p>	

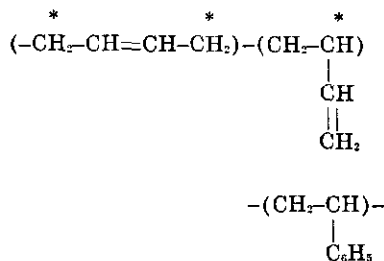
agents that yield free radicals on oxidation. Examples are shown in Table 1.

The interaction of polymers with curing agents is possible because of the reactivity conferred by the ethylenic unsaturation. The ally-

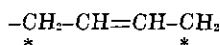
Natural rubber, isoprene rubber:



SBR:



Butadiene rubber:



lic or hydrogen atoms (marked with the double asterisk) are the most reactive; those bearing a single asterisk are less so. Natural rubber is more rapidly vulcanized than are the butadiene polymers because of the activating effect of the methyl group.

It is essential that only a limited amount of cure occur during the mixing, storage, and tire-building steps. The crosslinking or vulcanization must begin after the item is molded and it must stop when the desired state of cure is reached.

Thus, the compounding of a vulcanizable rubber for commercial use includes the addition of supplementary materials along with the curing agent. These serve a number of roles in optimizing final properties.

Cure accelerators or cure retarders are added to control the rate of cure, adapting it to give the desired state of cure and the best final properties at the temperature achieved. These additives may be inorganic, organic, or mixtures. They do not significantly change the chemical modification achieved during vulcanization but, instead, control the rate.

A change in the curing system in addition to altering the nature and balance of the reactions occurring during vulcanization can also affect the oxidation stability of the network. Choice of crosslinking system can vary combinations of C-C and C-S_x-C bonds. In the more complex case of synthetic rubbers, the crosslinking efficiency increases with vinyl content, apparently due to the markedly different reactivity of 1,2 as compared with 1,4 units. Thus the network structure of synthetics becomes more complex.

In addition to the vulcanization systems, a commercially compounded stock may contain a number of other ingredients, depending on the ultimate use of the product (11): (1) processing aids (plasticizers, such as oils, softeners, or peptizers); (2) antioxidants to prolong product life; (3) antiozonants to reduce ozone damage; (4) reinforcing agents, normally carbon black; (5) fillers.

The reinforcing action of carbon black can be improved by high-temperature mastication and by adding certain chemicals (e.g., sulfur, organic sulfur compounds, dinitrosobenzene, quinone dioxime) to the mix (12). An increasing number of bonds form between the rubber and the carbon black surface. It is difficult to measure precisely the amount of interaction between the rubber and black without being confused by crosslinking of the rubber itself. Polymeric free radicals on the surface of the black, possibly through surface groups such as quinones or the polynuclear aromatic layer molecules, may be formed during mastication or thermal or oxidative aging. These make direct observation of the filler-rubber interaction most difficult.

Extrusion and Calendering

Extrusion and calendering are really modifications of the mill mixing step wherein the compounded rubber is exposed to heat and air for a relatively short time. By this time the stock is fully compounded, and the presence of antioxidants and antiozonants significantly reduces the sensitivity to oxygen.

Reclaimed Rubber

Rubber is reclaimed by being ground as fine as is economically feasible, separated from fi-

ber and metal, if possible, and heated in steam in the presence of reclaiming agents (acids, alkalis, inorganic salts). Six routes are available for commercial use, depending on the type of scrap available and the economics of the reclaiming process compared with the cost of new rubbers (9).

Reclaiming cannot be considered the reverse of vulcanization, for none of the combined sulfur is removed from the compound as "devulcanization" occurs. It has been postulated that a break develops in the crosslinked molecule to form a shorter chain. At the same time, additional double bonds develop and become available for further sulfur crosslinking. This new vulcanization will normally attack the rubber molecule at the double bond. Thus, the vulcanized scrap rubber has a different chemical make-up from cured virgin rubber.

The production of a uniform reclaim depends on the fineness of the ground rubber (increasingly costly) and whether the metal and/or fiber can be removed prior to the reclaiming step itself. Prior to World War II, natural rubber predominated in scrap being reclaimed. The introduction of an increasing number of synthetic rubbers into tires has greatly complicated the picture requiring the development of new reclaim processes. This has further been complicated as new fibers (nylon, polyester, glass, steel) replaced cotton and rayon.

In recent years the price and availability of natural and synthetic rubbers and the increasing cost of reclaim rubber have severely limited the role of reclaim in tire production and the output of reclaim has decreased.

Possibly, reclaimed rubber may assume a new importance as feed stock becomes less available and more costly, but a tight supply situation must be encountered to force such a change.

Disposal

There are several possible ways of disposing of scrap rubber (13, 14). Those not involving any chemical reaction are: burial, whole or in chopped form; grinding for use to improve soil; discarding in reefs for fish protection; grinding for use as a filler in rubber compounds; dissolving in oil for subsequent carbon black manufacture. Methods in which no chemical product is recovered are disposed of by

burning or by burning in a special furnace for production of steam.

A third method, pyrolysis for production of gas, oil, or black, is the one method of tire disposal which is related to the subject of this paper; the other routes do not involve chemical changes.

A joint program between Firestone and the Bureau of Mines explored the pyrolysis of scrap tires under a range of conditions selected to maximize gas or oil. The tires were shredded to various sizes ranging from 35 mesh to 3-in. pieces, and pyrolysis was conducted in the presence and absence of fabric and beads.

The Bureau of Mines-American Gas Association pilot plant was equipped with a retort in an electric furnace and a series of traps to separate readily condensable liquids from gaseous products (15).

Pyrolysis temperatures ranged from 140 to 926°C; a temperature of 500°C was chosen for high yields of liquid, and 900°C was used for increased gas yields (Table 2). Variations in

Table 2. Products obtained from pyrolysis of passenger tires.

	Products, wt-%	
	500°C	900°C
Residue	41.6	55.4
Heavy oil	44.0	13.2
Light oil	3.6	6.0
Liquor	2.9	2.2
Free ammonia	0.2	0.1
Gas	5.0	19.4
Total	97.1	96.3

the particle size and the presence of fabric had little effect on product yields. Residue in-

Table 3. Products obtained from pyrolysis of truck tires.

	Product, wt-%	
	500°C	900°C
Residue	36.5	55.2
Heavy oil	48.7	17.0
Light oil	4.3	5.0
Liquor	1.0	0.7
Free ammonia	0.2	0.1
Gas	5.0	19.2
Total	95.7	97.2

creased with increasing pyrolysis temperature; the yield of heavy oil decreased at the same time, and the amount of gas increased.

The lower yield of residue from truck tires pyrolyzed at 500°C (Table 3) was attributed to the greater content of natural rubber. The black residue was found to contain 7.0–15.3% ash, significantly higher than carbon blacks used in tire manufacture, and the quality was inferior.

The light oil condensed at -70°C was subjected to gas chromatographic analysis, and 61 components were identified. Most of the components were eluted prior to 2,4-dimethylpentane. Oil from the 500°C run eluted relatively more saturated and less unsaturated hydrocarbons than did the higher temperature runs (Table 4).

Table 4. Analysis of off-gas from 500°C pyrolysis.

Gas	Gas, vol-%
Hydrogen	51.8
Methane	18.9
Ethane	18.7
Propane	5.3
Propylene	3.0
Isobutane	0.5
Butane	0.5
Butene-1	0.2
Isobutylene	0.9
Trans-butene-2	0.1
Cis-butene-2	0.1
	100.0

The heavy oils were submitted to a spectrometric analysis and a number of probable components were proposed. Alkylbenzenes and alkylnaphthenes were the predominant components. Probable compounds identified from mass spectra included alkylbenzenes, phenols, 3-ring aromatics, biphenyl, acenaphthene, alkylnaphthalenes, phenols, 3-ring aromatics, biphenyl, acenaphthene, alkylnaphthalenes, indenes, styrene, alkylstyrenes, and/or indans.

Product from a 900°C pyrolysis contained from aromatic compounds than did the fraction from 500°C runs (Table 5).

Table 5. Gases from pyrolysis.

	500°C		900°C	
	BTU/CF ^a	CO ₂ % total gas	BTU/CF ^a	CO ₂ % total gas
Passenger tires	892	15.0	729	1.5
Truck tires	1,145	11.3	695	0.8

^a Stripped of light oil, CO₂ and saturated with water vapor.

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